# PHOTOCATALYTIC DEGRADATION PROCESS OF WASTE WATER USING TITANIUM DIOXIDE AS CATALYST

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**"I hereby declare that this thesis entitled "*Photocatalytic Degradation Process of Waste Water using Titanium Dioxide as Catalyst*" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidate of any other degree".**

**Signature : ……………………………………………**
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**Date : ……………………………………………**

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## ABSTRACT

Photocatalytic degradation is a process where the organic contaminant in water is degraded by UV light. UV photo oxidation acts to degrade and remove organic compound through the ultraviolet radiation to activate the catalyst. The catalyst used in this study is titanium dioxide ($TiO_2$) which is chosen based on its properties that are low toxicity, low resistance to corrosion and semiconductor. The semiconductor will absorb the UV light and attract electrons across the energy gap into the conduction band. This electron will change into hydroxyl radicals which can decompose organic compounds while still in the waste water stream. So this is the basic concept that applied in industrial to treat the waste water or any pollutant in water in order to protect the environmental. Simulated oils waste water was used to replicate the Palm Oil Mill Effluent (POME). The studied parameters are the effect of catalyst concentration and irradiation time. The effect of both parameters has studied using Design Expert 7 to determine the optimum condition of degradation activities. The degradation activities were measured through the change of initial and final COD and dissolved oxygen in sample. Through Analysis of Variance (ANOVA) and optimization application of Design Expert 7, it was found that the optimum condition to achieve maximum degradation activities.

# ABSTRAK

Penggunaan teknologi proses penguraian sisa air merupakan kaedah yang terbaik untuk merawat sisa buangan air. Teknologi proses penguraian ini adalah dimana bahan organik di dalam air akan di uraikan menggunakan sinaran ungu, (UV). Sinar UV ini bertindak sebagai penyingkir untuk menyingkirkan bahan organik melalui sinaran ungu untuk mengaktifkan pemangkin. Pemangkin yang digunakan ialah titanium dioksida ($TiO_2$) dimana ia mempunyai sifat-sifat seperti kurang toksik, tidak mudah terhakis dan semikonduktor. Semikonduktor akan bertindak menyerap sinar UV dan di situ berlakunya mekanisme dimana elektron akan berubah kepada ion hidroksida yang radikal yang mampu menguraikan bahan organik. Inilah konsep yang diguna pakai dalam industri untuk merawat sisa air buangan atau apa sahaja sisa untuk memelihara alam sekitar. Sampel disediakan dengan kepekatan yang sama dengan kepekatan sisa buangan dari kilang sawit (POME). Parameter yang dikaji ialah kesan kepekatan pemangkin dan masa sinaran UV terhadap aktiviti penguraian dan kedua-dua parameter ini dianalisis menggunakan perisian Design Expert 7 dalam menentukan aktiviti yang optimum untuk aktiviti penguraian. Aktiviti penguraian ini diukur melalui perbezaan COD awal dan COD akhir sample dan perubahan oksigen terlarut didalamnya. Melalui analisis varian (ANOVA) dan optimism dari perisian Design Expert 7 telah menemukan keadaan yang optimum untuk mencapai aktiviti penguraian yang maksimum.

# TABLE OF CONTENTS


| CHAPTER | TITLE | PAGE |
|---|---|---|
| | **DECLARATION** | **ii** |
| | **ACKNOWLEDGEMENT** | **iii** |
| | **ABSTRACT** | **iv** |
| | **ABSTRAK** | **v** |
| | **TABLE OF CONTENTS** | **vi** |
| | **LIST OF TABLES** | **ix** |
| | **LIST OF FIGURES** | **x** |
| | **LIST OF SYMBOLS** | **xi** |
| | **LIST OF APPENDICES** | **xii** |
| **1** | **INTRODUCTION** | **1** |
| | 1.1 Research Background | 1 |
| | 1.2 Problem Statement | 3 |
| | 1.3 Objective of Research | 3 |
| | 1.4 Scope of Research | 4 |
| | 1.5 Rational and Significant of Research | 4 |
| **2** | **LITERATURE REVIEW** | **6** |
| | 2.1 Photocatalytic Degradation | 6 |
| | 2.2 Titanium Dioxide as Photocatalyst | 7 |
| | 2.3 Mechanism of Titanium Dioxide | 8 |
| | 2.4 Waste Water Remediation | 9 |
| | 2.5 Palm Oil Mill Effluent | 10 |

| | | | |
|---|---|---|---|
| | 2.6 | Measurement of Water Quality | 11 |
| | | 2.6.1 Dissolved Oxygen | 11 |
| | | 2.6.2 Chemical Oxygen Demand | 13 |
| | 2.7 | Department of Environment Water Quality Index Classes | 13 |
| **3** | **METHODOLOGY** | | **16** |
| | 3.1 | Material | 16 |
| | 3.2 | Equipment | 16 |
| | 3.3 | List of Equipment | 17 |
| | 3.4 | Reagent and Chemical | 20 |
| | 3.5 | Design of Experiment Set-Up | 21 |
| | | 3.5.1 Effect of Irradiation Time and Catalyst Concentration | 21 |
| | 3.6 | Analysis | 22 |
| **4** | **RESULT AND DISCUSSION** | | |
| | 4.1 | Introduction | 23 |
| | 4.2 | Effect of Irradiation Time and Catalyst Concentration toward Degradation Process | 24 |
| | 4.3 | Effect of Irradiation Time and Catalyst Concentration toward Dissolved Oxygen Change. | 26 |
| | 4.4 | Photodegradation Activity Optimization | 28 |
| **5** | **CONCLUSION** | | |
| | 5.1 | Conclusion | 30 |
| | 5.2 | Recommendations | 30 |

**REFERENCES** 32

**APPENDICES** 35

## LIST OF TABLE


| TABLE | TITLE | PAGE |
|---|---|---|
| 2.1 | Solubility of Oxygen in Water | 12 |
| 2.2 | Water Quality Index | 14 |
| 2.3 | General Rating Scale for the Water Quality Index | 15 |
| 4.1 | Result of Experiment | 23 |

## LIST OF FIGURES


| FIGURE NO | TITLE | PAGE |
|---|---|---|
| 3.1 | Dissolved Oxygen Meter | 17 |
| 3.2 | High Range COD Reagent | 18 |
| 3.3 | HACH Spectrophotometer | 18 |
| 3.4 | COD Digester | 19 |
| 3.5 | Set up of the experiment photodegradation | 20 |
| 3.6 | Simplified Flow Diagram of Experiment | 21 |
| 4.1 | Graph of Interaction between Catalyst Concentration and Irradiation Time toward Degradation Activity | 25 |
| 4.2 | Graph of Interaction between Catalyst Concentration and Irradiation Time toward Dissolved Oxygen in Sample | 26 |
| 4.3 | Desirability graph | 28 |
| 4.4 | Desirability Chart | 29 |

## LIST OF SYMBOLS

| | | |
|---|---|---|
| COD | - | Chemical Oxygen Demand |
| DO | - | Dissolved Oxygen |
| $TiO_2$ | - | Titanium Dioxide |
| UV | - | Ultra Violet |
| PCA | - | Photocatalytic Activity |
| WQI | - | Water Quality Index |
| DOE | - | Department of Environment |

# LIST OF APPENDICES


| APPENDIX | TITLE | PAGE |
|---|---|---|
| A | Analysis of variance ( ANOVA) for degradation | 35 |
| B | Analysis of variance ( ANOVA) for dissolved oxygen | 41 |
| C | Attachment of Figures | 48 |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by either human activities or industrial activities, which can be harmful to organisms and plants which live in these water bodies. It has always been a major problem to the environment. With industrialization in major areas and an urban city growing the water around them just keeps getting polluted. A lot of water pollution is caused by factories near rivers and lakes doing illegal dumping.

One type of water pollution is Palm oil mill effluent (POME) that contains high concentration of organic matter. COD concentration is in the range of 45,000 to 65,000 mg/l, 5-day BOD 18,000 to 48,000 mg/l and oil and grease greater than 2,000 mg/l. The COD: N: P ratio is around 750:7.3:1 (K.K. Chin, S.W. Lee, H.H. Mohammad, 1996).

On average, about 0.1 tonne of raw Palm Oil Mill Effluent (POME) is generated for every tonne of fresh fruit bunch processed. POME consists of water soluble components of palm fruits as well as suspended materials like palm fiber and oil. Despite its biodegradability, POME cannot be discharged without first being treated because POME is acidic and has a very high biochemical oxygen demand (BOD).

One of the methods found in photocatalytic degradation is a process where the organic contaminant in water will be degraded by using the UV light. Photocatalytic oxidation is one of the most effectively clean technologies for the degradation of waste water and any pollutants or contaminant in water. However, the application of heterogeneous photocatalytic for waste water treatment on an industrial scale has been impeded by a lack of mathematical models that can be readily applied to a reactor design and scale up (Gianluca Li Puma and Po Lock Yue, 2002).

UV photo-oxidation acts as eliminator to removing organic compound through the ultraviolet radiation to activate the catalyst. The catalyst that will use in this method is titanium dioxide ($TiO_2$) which is consider to it's properties that have low toxicity, low resistance to corrosion and semiconductor. The semiconductor will absorb the UV light and attract electrons across the energy gap into the conduction band. This electron will change into hydroxyl radicals which can decompose organic compounds while still in the waste water stream. So this is the basic concept that applied in industrial to treat the waste water or any pollutant in water in order to protect the environmental.

The purpose of this research is to study about the effects of temperature and irradiation time of the waste water towards the photodegradation process by measuring the chemical oxygen demand (COD) value and dissolve oxygen (DO) value. COD is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. COD measurements are commonly made on samples of waste water or of natural water contaminated by domestic or industrial wastes in order to protect the quality of water. Chemical oxygen demand is measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant under specific conditions of temperature and for a particular period of time.

## 1.2 Problem Statement

The growth of the industrial field and development of country especially in economic and investment give the huge effect to our environment including organisms and plant. However, in contexts of environmental awareness, there are still several authorities and people who are irresponsible in protect the environment from any pollution. Besides that the primary and secondary treatment of POME seems not much efficient because its still have the higher value of COD, BOD and the others composition that can harm marine life. The purpose of this research is to venture the tertiary treatment in addition to secondary and primary treatment to further to reduce the COD and BOD value in order to protect the environment. This technology process must be developed in order to enhance treatment in an industrial scale instead of laboratory scale.

## 1.3 Objective

The objectives of this research are

1. To study the effect of time irradiation of UV light towards degradation activities.
2. To study the effect of catalyst concentration towards the photocatalytic degradation.

## 1.4 Scope of Research

This study will concentrate on determining the effect of temperature and time irradiation towards the photocatalytic degradation process. The equipment that use in this experiment is COD digester and UV lamp. The function of COD digester is to determine the initial COD value of waste water prior to catalyst addition and the final value after irradiation with catalyst, $TiO_2$.

- For the time irradiation, we use the UV lamp to emit to the sample in certain time at range 0 to 150 minutes.
- The catalyst concentration that used for this experiment is between 0 to 2.5mg/L
- The value of COD will be measured using COD digester and the oxygen consumed is measured by using the DO (dissolve oxygen) meter.

## 1.5 Rational and Significant

The rational of this research is to study potential of a new technology that can be developed and applied for waste water treatment. Relating to the current situation that our industrial activities are growing every year, the production of waste water also must be consider in order to protect the environment, resident and especially marine life from the hazardous waste. For the further research and development, the study potential of this process can be applied to treat the contaminant and pollutant waste water at industry which is more hazardous than POME. Photocatalysis on $TiO_2$ represents a promising alternative technology for degradation of organic pollutant and inactivation of microorganisms in water through the photogeneration of separated electrons and positive holes in semiconductor particles (Josef Krysa *et al.*, 2005). In this research, the photocatalytic degradation process is expected to produce the simplest and non-toxic product which is carbon dioxide ($CO_2$) and water ($H_2O$) respectively. Using the interaction between ultraviolet radiation and titanium dioxide ($TiO_2$) has a strong potential for destruction of toxic in water (Sixto Malato Rodriguez *et al.*, 1996).

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Photocatalytic Degradation

Photocatalytic degradation process is an eliminating process of organic compound in water by using the interaction between ultraviolet radiation and titanium dioxide ($TiO_2$) as catalyst. It has the potential for treating of toxic organics in waste water. While UV photo-oxidation is a destructive method of removing organic compounds, like oil, that uses ultraviolet radiation to activate a catalyst. (Alexia Patsoura *et al.*, 2007).

In the last few years, research on new methods for advanced waste water treatment has gone from processes involving phase transfer of a contaminant (e.g. activated carbon, air stripping, pyrolysis) to complete destruction of the contaminant. The possible application of photocatalytic for destruction of the organic mater in water has been extensively investigated. (Ollis et *al.*, 1991; Matthews, 1991). It has been found that the production of $CO_2$ and $H_2$ from this process. The problem with toxic organic compounds in waste water is becoming an increasing threat to people's health.

UV photo-oxidation does not require a separation step to remove the contaminant because the organic contaminant is destroyed while still in the waste water stream. (Jauregui *et al.*, 1998). This eliminates the costs and time associated with this additional step. There are three different oxidizers are currently used in industry, UV light, hydrogen peroxide and ozone. .

## 2.2 Titanium Dioxide as a Photocatalyst

Titanium dioxide is attractive because of this ability and because of its low toxicity and resistance to corrosion (Alfano *et al*., 1970). Titanium dioxide is considered a semiconductor because it takes UV light to promote electrons across the energy gap into the conduction band. These electrons may then form hydroxyl radicals, which can decompose organic compounds. Many studies have been published on the use of $TiO_2$ as a photocatalyst for the decomposition of organic compounds. $TiO_2$ is active under UV light. Photocatalytic activity (PCA) is the ability of a material to create an electron hole pair as a result of exposure to ultraviolet radiation. The resulting free-radicals are very efficient oxidizers of organic matter. Photocatalytic activity in $TiO_2$ has been extensively studied because of its potential use in sterilization, sanitation, and remediation applications.

Titanium dioxide, particularly in the anatase form, is a photocatalyst under ultraviolet light. Recently it has been found that titanium dioxide, when spiked with nitrogen ions, or doped with metal oxide like tungsten trioxide, also act as photocatalyst under visible and UV light. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly. It is also used in the Graetzel cell, a type of chemical solar cell (Xu Zhao *et al*., 2007; Efthalia C. *et al*., 2007; C. Fotiadis *et al*., 2007; A.R. Mohamed *et al*., 2004; Heqing Tang et al., 2008).

The photocatylic properties of titanium dioxide were discovered by Akira Fujishima in 1967. The process on the surface of the titanium dioxide was called the Honda-Fujishima effect. Titanium dioxide has potential for use in energy production:

as a photocatalyst, it can carry out hydrolysis for example break water into hydrogen and oxygen. Were the hydrogen collected, it could be used as a fuel. The efficiency of this process can be greatly improved by doping the oxide with carbon, as described in "Carbon-doped titanium dioxide is an effective photocatalyst" produce electricity when in nano particle form. Research suggests that by using these nano particles to form the pixels of a screen, they generate electricity when transparent and under the influence of light. If subjected to electricity on the other hand, the nano particles blacken, forming the basic characteristics of a LCD screen. According to creator Zoran Radivojevic, Nokia has already built a functional 200-by-200-pixel monochromatic screen which is energetically self-sufficient (Masaaki Kitano *et al.*, 2007)

As $TiO_2$ is exposed to UV light, it becomes increasingly hydrophilic; thus, it can be used for anti-fogging coatings or self-cleaning windows. $TiO_2$ incorporated into outdoor building materials, such as paving stones in noxer blocks or paints can substantially reduce concentrations of airborne pollutants such as volatile organic compounds and nitrogen oxides

## 2.3 Mechanism of $TiO_2$

The photocatalytic reaction proceeds via a series of chemical events following the initiation step of pair electron hole formation. This leads to the utilization of both the electron hole, $h^+$ for oxidation processes and eventually to the capture of the $e^-$ electron for reduction processes, as well as the potential formation of super oxides anions and hydrogen peroxide from oxygen (Hugo de Lasa *et. al.,* 2005).

Unfortunately, there is a competing electron and electron hole recombination step the reverse of equation (1-1), and this result in process inefficiencies and the waste of energy supplied by the photon. The electron hole recombination can be considered as one of the major factors limiting the efficiency of the photocatalytic processes. (Hugo de Lasa *et. al.,* 2005).

$$photocatalyst \rightarrow e^- + h^+ \tag{2.1}$$

Every effort to prevent electron and electron hole recombination will improve the efficiency of photocatalytic processes and will considerably help to achieve the application of this technique for water purification (Hugo de Lasa *et. al.,* 2005).

The photocatalytic reaction can be represented as a number of mechanistic steps (M. Saquib *et. al.,* 2007). A photo excited $TiO_2$ generates an electron and an electron hole.

$$TiO_2 \overset{hv}{\rightarrow} e^- + h^+ \tag{2.2}$$

Electron transfer from the adsorbed substrate ($RX_{ad}$), absorbed water or the $OH_{ad}$ ion to the electron hole.

$$h^+ + RX_{ad} \rightarrow RX_{ad}^+ \tag{2.3}$$

$$h^+ + H_2O_{ads} \rightarrow O_{ads}^{\bullet} + H^+ \tag{2.4}$$

$$h^+ + OH_{ad}^- \rightarrow OH_{ad}^{\bullet} \tag{2.5}$$

## 2.4 Wastewater Remediation

Photocatalytic degradation and $TiO_2$ as photocatalyst offers great potential as an industrial technology for detoxification or remediation of wastewater due to several factors such as the process occurs under ambient conditions very slowly, direct UV light exposure increases the rate of reaction, the formation of photocyclized intermediate products, unlike direct photolysis techniques, is avoided, oxidation of the substrates to $CO_2$ is complete, the photocatalyst is inexpensive and has a high turnover and lastly $TiO_2$ can be supported on suitable reactor substrates.

## 2.5 Palm Oil Mill Effluent (POME)

Palm oil mill effluent (POME), from a factory site in India contained about 250,000 mg/L chemical oxygen demand (COD), 11,000 mg/L biochemical oxygen demand, 65 mg/L total dissolved solids and 9000 mg/L of chloroform-soluble material. Treatment of this effluent using Yarrowia lipolytica NCIM 3589, marine hydrocarbon-degrading yeast isolated from Mumbai, India, gave a COD reduction of about 95% with a retention time of two days. Treatment with a chemical coagulant further reduced the COD and a consortium developed from garden soil clarified the effluent and adjusted the pH to between 6 and 7. The complete treatment reduced the COD content to 1500 mg/L which is a 99% reduction from the original. Palm oil mill effluent (POME) is an important source of inland water pollution when released into local rivers or lakes without treatment. POME contains lignocellulolic wastes with a mixture of carbohydrates and oil (N.Oswal *et al*, 2001).

Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of POME are very high and COD values greater than 80,000 mg/L are frequently reported. Incomplete extraction of palm oil from the palm nut can increase COD values substantially. POME has generally been treated by anaerobic digestion resulting in methane as a value added product (Sinnappa, 1978; Borja *et al.,* 1995). The raw POME may also be used in crop irrigation (Wood *et al.* 1979) and treated it using a pond system (Chin *et al*., 1996). The aerobic digestion of POME decreases carbon content and inorganic nitrogen and changes pH from the acidic range to an alkaline one (Agamuthu *et al.*, 1986). Such treatment also increases the ratio of organic nitrogen leading to the production of a better fertilizer.

The sample palm oil mill effluent (POME) can be treated using other process which is membrane technology but it require a lot of process and it maintenance and fouling which will increase overall cost of plant. Waste water treatment is one of the most important components in POME because the facility to treat it is being generated in large volume during the production of crude palm oil (CPO) (Chin *et al*., 1996).

## 2.6 Measurement of Water Quality

The complexity of water quality as a subject is reflected in the many types of measurements of water and Wastewater quality indicators. These measurements include (from the simplest and basic to more complex):

- Dissolved Oxygen(DO)
- Chemical oxygen demand (COD)

### 2.6.1 Dissolved Oxygen (DO)

Dissolved oxygen analysis measures the amount of gaseous oxygen ($O_2$) dissolved in an aqueous solution. Oxygen gets into water by diffusion from the surrounding air, by aeration (rapid movement), and as a waste product of photosynthesis. When performing the dissolved oxygen test, only grab samples should be used, and the analysis should be performed immediately. Therefore, this is a field test that should be performed on site.

Adequate dissolved oxygen is necessary for good water quality. Oxygen is a necessary element to all forms of life. Natural stream purification processes require adequate oxygen levels in order to provide for aerobic life forms. As dissolved oxygen levels in water drop below 5.0 mg/l, aquatic life is put under stress. The lower the concentration, the greater stress. Oxygen levels that remain below 1-2 mg/l for a few hours can result in large fish kills. Measure DO in water sample by using Winkler test, oxygen probe or by iodometric titration. DO is inversely proportional to temperature, and the maximum amount of oxygen that can be dissolved in water at 0°C is 14.6 mg/L.

**Table 2.1** Solubility of Oxygen in Water
(Ruth F.W. and Robin M, 4th edition)

| Water Temperature (°C) | Saturation concentration of oxygen in water (mg/L) |
|---|---|
| 0 | 14.6 |
| 2 | 13.8 |
| 4 | 13.1 |
| 6 | 12.5 |
| 8 | 11.9 |
| 10 | 11.3 |
| 12 | 10.8 |
| 14 | 10.4 |
| 16 | 10.0 |
| 18 | 9.5 |
| 20 | 9.2 |
| 22 | 8.8 |
| 24 | 8.5 |
| 26 | 8.2 |
| 28 | 8.0 |
| 30 | 7.6 |

Based on the table 2.1 shows that when the temperature increases the concentration of oxygen in water will decrease. This is because the temperature will affect the amount of oxygen in water. Related to this research when the temperature of waste water is high the degradation process will decrease because the oxygen present in the sample is less. This DO value also related to the COD value in order to determine the photodegradation process.

### 2.6.2 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. COD measurements are commonly